

# STABILIZERS FOR TITANIUM DIBORIDE-CONTAINING CATHODE STRUCTURES

## Field of the Invention

The invention generally relates to stabilizing  
5 additives for titanium diboride-containing carbonaceous  
cell components for metal reduction cells, e.g. cell  
cathodes and processes for their preparation.

## Background of the Invention

10 Metal reduction cells, such as those used for  
producing aluminum, typically utilize carbonaceous  
cathodes. The cathode can be in the form of a layer  
formed on the inside of the reduction cell, for example,  
as an array of a cathode blocks joined by ramming paste.  
15 However, over time, electrolyte in the cell and the  
molten metal tend to attack the carbon-based cathode,  
causing it to erode. The erosion is further enhanced by  
movements in the cell due to magneto-hydrodynamic  
effects. Similar erosion also occurs to the ramming  
20 pastes used to seal cracks and joints in the cell.

It has been known for a number of years that  
cathodes can be made from a composite of a carbon-  
containing component and a metal boride, such as  
titanium diboride( $\text{TiB}_2$ ). The  $\text{TiB}_2$  helps to protect the  
25 cathode against erosion and oxidation and makes the  
cathode wettable to aluminum. The wettability is an  
important characteristic particularly in drained cathode  
cells.

Attempts have been made to apply refractory  
30 coatings made of metal borides, such as titanium boride  
( $\text{TiB}_2$ ), to a cathode to protect it from erosion. An  
example of such coating is described in WO 01/61077, in

which the coating was made from a refractory slurry of titanium boride dispersed in an aluminum oxalate complex. However, differences in thermal expansion between the coating and the cathode often cause the coatings to crack or dislodge from the cathode.

Another solution to cathode erosion is described in WO 00/36187 where composite cathodes blocks are formed, in which metal boride layers are bonded to a carbonaceous substrate to form a multi-layer cathode block. The carbonaceous substrate is given a roughened surface so that the metal boride layer may better bond to the carbonaceous substrate.

Since metal borides used in making cathode blocks are very expensive, another method of manufacturing the blocks is to mix metal boride precursors of, for example, metal oxides and boron oxides, with the carbonaceous substrate to produce a composite material that forms metal boride in situ when exposed to molten aluminum in the cell, or when it is exposed to the heat of the cell at start-up and during operation. An example of such a process is described in WO 00/29644.

Although use of cathode blocks containing metal borides in reduction cells reduces the extent of cathode erosions, lab and factory experiments show that metal boride particles gradually leach out of the cathodes and enter a film of liquid aluminum present on the surface of the cathode. In industrial use, this leads to the formation of a metal boride-aluminum layer, having a thickness of approximately 3mm, on the cathode. In the case where titanium boride is used in the cathode block the layer is a  $TiB_2$ -Al(l) layer. The removal of  $TiB_2$  particles leads to a contamination of the metal product and to a progressive erosion of the cathode blocks,

since the more metal boride that leaches out of the cathode, the more quickly the cathode erodes.

It is therefore desirable to find an inexpensive and simple way of preventing leaching of metal borides from carbonaceous composite cathode blocks, refractory coatings and ramming pastes.

It is also desirable to make erosion-resistant, aluminum wettable, cathode blocks, refractory coatings and ramming pastes which do not leach out metal borides during use.

#### Summary of the Invention

The present invention relates to a novel additive to be included in a carbonaceous material-TiB<sub>2</sub> aggregate mixture used in the production of metal reduction cell components, such as cell cathodes. The additive comprises an intimate mixture of two finely divided compounds which is added to the aggregate. At least one of the additive compounds has a melting point higher than both the baking temperature for the cathodes and the melting temperature of aluminum. Once the electrode has been formed and baked, the additive is generally found in a carbon matrix between the TiB<sub>2</sub> particles. During aluminum reduction, liquid aluminum wets the cathode surface and penetrates the cathode via open pores. In the pores, the liquid aluminum reacts with the additive mixture to form a dense phase that seals the open pores of the cathode and stabilizes the carbon matrix around the TiB<sub>2</sub> particles of the carbon-TiB<sub>2</sub> aggregate.

The present invention thus provides in one embodiment, a method of making an aluminum reduction cell component having a physical and chemically stable

surface that comprises mixing together a carbonaceous material,  $TiB_2$  and up to 25% by weight of a finely divided additive consisting of a combination of two intimately mixed compounds and forming and baking the mixture into the cell component, wherein at least a first of the two compounds has a higher melting temperature than the baking temperature. Thereby, when the cell component is contacted with molten aluminum, the aluminum reacts with the additive to form a dense phase at the surface of the cell component, having low solubility in aluminum.

The present invention, in a further embodiment, provides a baked aluminum reduction cell component having a physical and chemically stable surface and comprising carbonaceous material,  $TiB_2$  and up to 25% by weight of a finely divided additive consisting of a combination of two intimately mixed compounds, positioned between particles of the  $TiB_2$  and reactable with molten aluminum to form a dense phase on the surface of the cell component, said dense phase having low solubility in aluminum. At least a first of the two compounds has a higher melting temperature than the baking temperature of the cell component.

The combination of two compounds can disperse evenly in the aggregate and can react with molten aluminum to form a dense phase on the surface of the cell components. The compounds are intimately mixed in the form of finely divided particles, such that particles of one compound come into contact with particles of the other compound. In this context, "finely divided" refers to particles typically having an average size of less than 200  $\mu m$ , preferably less than 100  $\mu m$ .

At least one compound of the additive mixture has a melting temperature greater than the baking temperature for the cell component, e.g. 1200°C or higher. A second compound may have a melting temperature higher or lower than the baking temperature for the cell component. When the second compound has a lower melting temperature, during the baking stage, the lower melting compound melts around the higher melting compound to form an agglomerate.

It is also possible to use two high melting compounds, neither of which melts during the baking stage. In this case, the two compounds remain in intimate solid contact throughout the baking stage and engage the molten aluminum in the aluminum reduction cell in that form.

The high melting compound is typically a titanium compound such as TiC or TiO<sub>2</sub>. However it is possible to use other high melting compounds that will react appropriately with the molten aluminum according to the invention, e.g. Al<sub>2</sub>O<sub>3</sub> or BN. The lower melting compound is typically a boron compound, such as B<sub>2</sub>O<sub>3</sub>, boric acid, etc. Where both compounds are high melting materials, it is preferred to use the combination of a high melting titanium compound and a high melting boron compound, such as boron carbide or boron nitride.

#### Brief Description of the Drawings

The present invention will be described in conjunction with the following figures:

Fig. 1 is a perspective view, partially cut-away, of a conventional aluminum reduction cell with which the present invention may be used;

Fig. 2 is a partial transverse cross-section of the cell of Fig. 1 on an enlarged scale showing the electrolyte and molten aluminum;

Fig. 3 is a micrograph illustrating a traditional cathode block, having no additives and showing leached  $\text{TiB}_2$  particles in the molten aluminum layer; and

Fig. 4 is a micrograph illustrating a cathode block comprising additives of the present invention and showing no  $\text{TiB}_2$  in the molten aluminum.

#### 10 Detailed Description of Preferred Embodiments of the Invention

With reference to Fig. 1, a conventional reduction cell 10 comprises cathode blocks 20, commonly made of a metal boride-carbon aggregate. The cathode blocks are separated by gaps 18, the gaps 18 being filled with ramming paste 21. As seen in Fig. 2, molten electrolyte 12 contacts the cathode 20 and the ramming paste 21 and a layer of molten aluminum 17 forms on the cathode 20. During operation, metal boride tends to leach out from the porous cathode block and intermingle with the layer of molten aluminum 17, causing contamination of the molten aluminum. Removal of metal boride from the cathode block also accelerates erosion of the cathode block.

25 It has been found that combining an additive mixture of two finely divided, intimately mixed compounds with the carbonaceous- $\text{TiB}_2$  aggregate used in making cathode blocks results in the additive reacting with molten aluminum in the reduction cell to form a dense phase at the surface of the cathode block. This dense phase reduces erosion of the cathode block.

In a preferred embodiment, the combination of two compounds of the additive mixture comprises one compound with a melting temperature higher than the cathode-baking temperature and one boron containing compound with a melting temperature lower than the cathode-baking temperature. When such a combination is intimately mixed and exposed to heat, the lower melting compound melts around the high melting compound to form an agglomerate. Suitable combinations of high melting and low melting compounds include  $\text{TiO}_2$  and  $\text{B}_2\text{O}_3$ ,  $\text{TiC}$  and  $\text{B}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{B}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{Na}_2\text{B}_4\text{O}_7$ ,  $\text{BN}$  and  $\text{B}_2\text{O}_3$ , and an  $\text{Al-C-Ti}$  master alloy and  $\text{B}_2\text{O}_3$ . In these combinations, it is also possible to replace the  $\text{B}_2\text{O}_3$  by  $\text{H}_3\text{BO}_3$ .

Other combinations of compounds suitable as the additive mixture include  $\text{TiO}_2$  with  $\text{BN}$  and  $\text{TiO}_2$  with  $\text{B}_4\text{C}$ . In such combinations, neither of the two compounds melt during the cathode-baking step, but are rather intimately mixed in their solid, powdered form.

A preferred combination comprises a titanium-containing high melting compound and  $\text{B}_2\text{O}_3$  as the lower melting compound. A most preferred combination is  $\text{TiO}_2$  and  $\text{B}_2\text{O}_3$ . Although all of the above-mentioned combinations are suitable additives, for illustrative purposes, the  $\text{TiO}_2$ - $\text{B}_2\text{O}_3$  combination shall be referred to in the rest of this description.

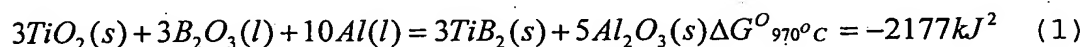
The additive mixture of  $\text{TiO}_2$ - $\text{B}_2\text{O}_3(\text{s})$  can be obtained via a method as described in International Publication No. WO 00/29644, incorporated herein by reference. The  $\text{TiO}_2$  and  $\text{B}_2\text{O}_3$  particles of the additive mixture are preferably less than 100 microns ( $\mu\text{m}$ ) and more preferable less than 30  $\mu\text{m}$ . The oxides are mixed in an approximately stoichiometric ratio and preferably in a ratio of 40-50% by weight  $\text{TiO}_2$  to 50-60% by weight  $\text{B}_2\text{O}_3$ .

The additive mixture is preferably a finely divided powder and may be prepared at room temperature.

A fine powder of the additive mixture is added to a cathode aggregate of  $TiB_2$  and carbon in an amount of preferably up to 10% by weight, e.g. 1 to 10% by weight. The aggregate generally consists of a mixture of 40-49% titanium diboride ( $TiB_2$ ), and 50% carbonaceous component. The carbonaceous component can be any carbonaceous components known in the art of cathode manufacture, for example a mixture of anthracite and pitch. During the mixing process, the powder is dispersed in the aggregate and, once the cathode has been formed and baked, the powder becomes positioned essentially in a carbon matrix between the  $TiB_2$  particles.

In operation, liquid aluminum wets the cathode and penetrates the cathode via open pores to depths ranging from 0.5 to 1 mm. During penetration, the aluminum reacts with  $TiO_2-B_2O_3$  to form, at  $970^\circ C$ ,  $TiB_2$  and  $Al_2O_3$  as described by equation 1 below:

20



The formation of a relatively stable solid phase of  $Al_2O_3$  in the presence of aluminum favours the sealing of open pores in the cathode and improves the performance of the cathode by stabilizing the carbon matrix around initial  $TiB_2$  particles. This reduces the rate at which  $TiB_2$  particles leach out of the cathode.

Products formed by other suitable combinations and molten aluminum are given in Table 1. These products also form a dense phase on the cathode surface:



Table 1

Additive Combination	Reaction Product with Molten Aluminum
TiC and B <sub>2</sub> O <sub>3</sub>	Al <sub>4</sub> C <sub>3</sub> , TiB <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , AlTi, Al <sub>3</sub> Ti or Ti <sub>3</sub> Al
Al <sub>2</sub> O <sub>3</sub> and B <sub>2</sub> O <sub>3</sub>	(Al <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> (B <sub>2</sub> O <sub>3</sub> )
TiO <sub>2</sub> and Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	TiB <sub>2</sub> , alumina with Na in solid solution
BN and B <sub>2</sub> O <sub>3</sub>	AlN, Al <sub>2</sub> O <sub>3</sub>
Al-C-Ti master alloy and B <sub>2</sub> O <sub>3</sub>	TiC, AlTi intermetallics, TiB <sub>2</sub> , Al <sub>4</sub> C <sub>3</sub>
TiO <sub>2</sub> and BN	TiB <sub>2</sub> , AlN, Al <sub>2</sub> O <sub>3</sub>
TiO <sub>2</sub> and B <sub>4</sub> C	TiB <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , Al <sub>4</sub> C <sub>3</sub>

Example 1:

Cathode blocks were prepared combining 33 wt% anthracite, 17 wt% pitch and 45 wt% TiB<sub>2</sub> to form an aggregate mixture. To this was added 5 wt% of the TiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> additive mixture in the form of a fine powder containing 30% -74µm particles. The pre-mixed additive was mixed with the aggregate at a temperature of about 160°C for about 45 minutes to form a hot paste.

The hot paste was then transferred to a mould fixed on a vibrating table. The vibrated block was baked at about 1100°C for about 2 hours.

Cathode blocks prepared in the above manner were subject to laboratory electrolysis testing for 65 hours. The results showed complete wetting of the cathode, along with a significant reduction in the removal of TiB<sub>2</sub> particles.

Fig. 3 and 4 show loss of TiB<sub>2</sub> particles after electrolysis for cathode blocks in which no stabilizing agents were added, (Fig. 3) and for the cathode blocks of Example 1 (Fig. 4). Fig. 3 clearly shows that TiB<sub>2</sub> particles have leached out of the cathode and into the

aluminum film. These particles are not present in the aluminum film of Fig. 4.

Use of the present invention is not limited to production of cathode blocks. The additive mixtures can  
5 also be used in producing ramming pastes, side wall blocks and in refractory coatings such as those disclosed in International Publication No. WO 01/61077, incorporated herein by reference. In the case of metal  
10 boride-containing ramming pastes, the additive mixture can be added to the paste aggregate, which usually also comprises anthracite, pitch, calcined coke or anode butts, and light oil diluents.